



Thermal Extraction of VOCs from Grapefruit Essential Oil and Fresh Grapefruit Peel with a CDS Pyroprobe

Application Note

Fragrance, Food & Flavor

Abstract

This application note demonstrates a quick temperature ramp technique to improve the focusing of VOCs in grapefruit essential oil.

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Introduction

The CDS Pyroprobe proportional–integral–derivative (PID) controller is an analog circuit designed to quickly ramp sample temperatures for rapid pyrolysis while avoiding temperature overshoot. A new feature in the 6000 Pyroprobe institutes a multi-ramp tool, which allows for up to 3 temperature ramps per method. This can be used to reach faster equilibration times at low temperatures, which helps in the analysis of VOCs without using a secondary focusing trap.

In this application, several sampling techniques were used to study both grapefruit essential oil and grapefruit peel. Direct thermal extraction of grapefruit essential oil was studied using both a single temperature ramp and a multi-temperature ramp. Compounds with retention times under 10 minutes are traditionally collected onto a secondary trap for refocusing. Due to a quick ramp technique used with the Pyroprobe multi-ramp feature, in conjunction with the Pyroprobe's low dead volume of under 30 μ L, early eluting compounds can be extracted directly to the GC-MS while retaining a sharp peak shape. The data obtained from the grapefruit oil was then compared to the aroma notes found in grapefruit peel using the Pyroprobe dynamic headspace (DHS) attachment.

Experimental

Due to its high viscosity, a syringe was not used for sampling. Instead, a drop of the oil was added to a Whatman Glass Fiber filter, and 1.50mm hole punch of the filter was easily dropped into a Drop-In-Sample Chamber (DISC) tube. This was analyzed using a multi-ramp, and compared to a single ramp directly to the GC-MS. Additionally, 1 gram of fresh grapefruit peel was added to a 25 mL test tube, which was placed in the DHS vessel attachment installed on a Pyroprobe 6200, which has a secondary focusing trap, interfaced to a GC-MS for multi-step dynamic headspace analysis at 80°C.



Single Ramp

Pyroprobe

DISC Chamber:

Final 1: 80°C 60s

Final 2: none

Interface: 300°C

Transfer Line: 325°C

Valve Oven: 300°C

Multi-Ramp

Pyroprobe

DISC Chamber:

Final 1: 1300°C 1.6s

Final 2: 80°C 60s

Interface: 300°C

Transfer Line: 325°C

Valve Oven: 300°C

Dynamic Headspace

Pyroprobe 6200 with DHS

DHS Vessel: 80°C 10min
Purge Gas: He 40mL/min

Trap Contents: Tenax
Trap Rest: 40°C
Trap Final: 300°C 3min
Transfer Line: 325°C
Valve Oven: 300°C

GC-MS
Column: 5% phenyl (30m x 0.25mm)
Carrier: Helium 1.25mL/min
50:1 split
Injector: 360°C
Oven: 40°C for 2 minutes
12°C/min to 320°C
hold 15min
Ion Source: 230°C
Mass Range: 35-600amu

Results & Discussion

Grapefruit essential oil, extracted from tiny glands in grapefruit peel, is frequently used in aromatherapy due to its aroma compounds containing health benefits such as relief of stress and anxiety, anti-microbial properties, and lowering of blood pressure. Direct (no sorbent trapping) thermal extraction of grapefruit essential oil was performed to study the effectiveness of the quick ramp technique which uses the multi-ramp tool. The proper combination of two temperature setpoints results a ramp to 80°C within 2 seconds. By using 1300°C with a time of 1.6 seconds for the first setpoint, the sample was heated at the most rapid rate to reach 80°C. Partial chromatograms of grapefruit essential oil, comparing the quick ramping with the multi-ramp feature, and a single ramp are presented in Figure 1. Peak widths decreased using the multi-ramp. For example, alpha-pinene had a width at half-maximum height (FWHM) of 0.04 minutes using the multi-ramp feature, compared to 0.35 minutes using a single ramp. This is a nearly nine-fold improvement of peak resolution. This shows that VOCs can be well resolved without need for trapping.

In addition to using the Pyroprobe to directly extract VOCs from essential oils, larger sample sizes can be studied with the Pyroprobe's DHS module. Because the headspace is continually renewed over a time limit, dynamic headspace has sensitivity advantages over static headspace. The aroma profile of essential oil would be expected to look similar to the aroma profile grapefruit peel, so DHS analysis of grapefruit peel was used to confirm the oil's authenticity. Like the essential oil, grapefruit peel had compounds such as alpha-Pinene, Ylangene,

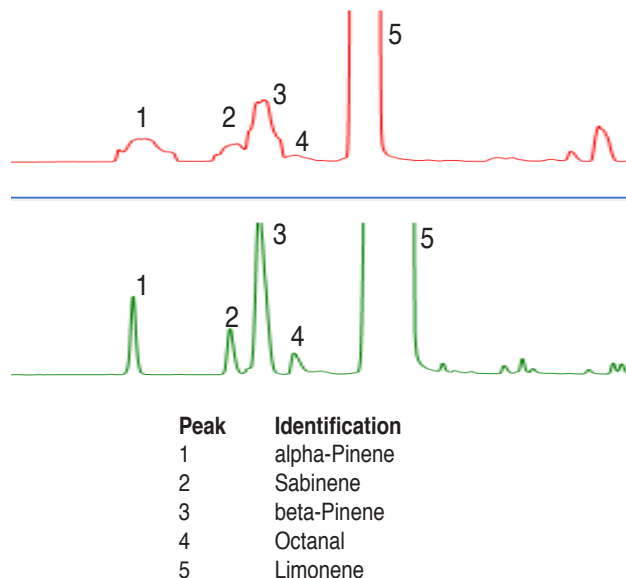


Figure 1. Direct Thermal Extraction Chromatograms of Grapefruit Essential Oil using a single ramp (top), and a multi-ramp (bottom).

Germancrene D, and Caryophyllene (Figure 2). Caryophyllene is also present in peppercorn¹ and is responsible for a “biting” quality. The overall profile of the grapefruit peel and the essential oil were nearly identical, confirming the authenticity of the essential oil.

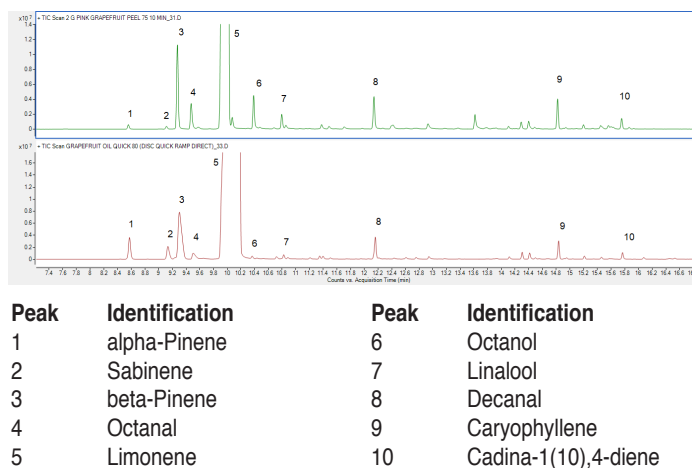


Figure 2. Dynamic Headspace of grapefruit peel, 80°C (top) compared to Quick Ramp Direct Thermal Extraction of grapefruit essential oil (bottom).

Conclusion

The Pyroprobe, while traditionally used for pyrolysis, is a versatile piece of equipment, lending itself to many techniques coupled with GC-MS analysis. Direct thermal extraction using the multi-ramp feature and dynamic headspace using the DHS attachment were highlighted in this application note.

References

1. K. Srinivasan , Black pepper and its pungent principle-piperine: a review of diverse physiological effects, Crit Rev Food Sci Nutr. 2007;47(8):735-48. doi: 10.1080/10408390601062054